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$KLi_3Fe(C_2O_4)_3$: a perovskite-like compound with 1:3 ordering at both A and B sites

Wenjiao Yao,[a] Yuanyuan Guo,[a] and Philip Lightfoot*[a]

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$KLi_3Fe(C_2O_4)_3$ adopts a perovskite-like structure with 1:3 ordering of (Li,Fe) on the B-site and (K,vacancy) on the A-site; there are no previous examples of this type of cation ordering in conventional perovskites.

Perovskites (generic formula ABX_3) continue to occupy centre-stage in solid state chemistry, as a source of both new materials with functional properties, and as a playground for novel compositional and structural variants[1]. The myriad structural variations on the perovskite theme are in part due to opportunities for forming cation-ordered (A and/or B sites)[2,3] or anion-ordered (X-site)[4,5] derivatives. In addition, hybrid perovskites, with molecular entities occupying the A and X sites, have recently been widely studied for potential ferroelectric or multiferroic properties.[6,7] In the latter materials, the X moiety is a bridging ligand, typically formate, cyanide, azide etc. These ligands therefore 'expand' the conventional perovskite framework, which has only monoatomic X species such as oxide or halide. The opportunities for structural variations within perovskites are therefore further enhanced by incorporation of such ligands. Oxalate is also a well-known ligand in the coordination polymer field, with a variety of possible linking and bridging modes.[8] Our recent exploratory studies of metal oxalate chemistry have led to several interesting new polymeric or framework materials of interest for electrochemical or magnetic properties.[9,10] In the present work we describe another new mixed metal oxalate, $KLi_3Fe(C_2O_4)_3$, which we show has an unexpected and highly novel relationship to the perovskite structure, in particular introducing a new structural variant involving simultaneous cation ordering at both the A and B sites.

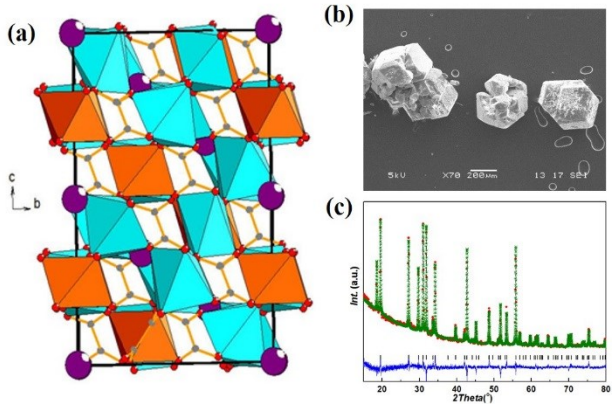

Figure 1. Characterisation of $KLi_3Fe(C_2O_4)_3$. (a) Crystal structure: FeO_6 octahedra orange, LiO_6 octahedra turquoise, K purple spheres, C grey. (b) SEM image of as prepared crystallites. (c) Rietveld refinement of powder XRD (295 K) in space group $R\bar{3}c$. a = 11.4420(2) Å, c = 15.1705 (3) Å. wR_p = 0.072, R_p = 0.0547, χ^2 = 1.836.

$KLi_3Fe(C_2O_4)_3$ was prepared using a self-flux hydrothermal method. Reactions were performed in a Teflon-lined autoclave at 190 °C for four days using commercially available $FeCl_2{\cdot}2H_2O$, oxalic acid, Li_2CO_3 and K_2CO_3 in molar ratio of 1.5:4:2:1 as starting reagents. A typical reaction yielded 80% of the title compound as a crystalline product based on Fe reactant. Trace amounts of a red impurity were easily removed manually. The resultant sample was highly pure, as supported by powder X-ray diffraction (XRD) and was used for further characterisation (*viz.* SEM morphology, thermogravimetric analysis (TGA), Fourier transformed infrared (FT IR) spectrum (see Figure 1 and electronic supplementary information, ESI). Single crystal XRD (173 K) revealed an apparently complex, but high symmetry structure, crystallising in space group $R\bar{3}c$, with a ~ 11.39, c ~ 15.12 Å (hexagonal setting). It can be noted that an isostructural compound $NH_4Li_3Fe(C_2O_4)_3$ has already been reported,[11] but in that case the structural description was set in the context of a coordination polymer network (3,4-connected ***pto*** net). That description is, of course, equally valid, but we believe that the relationship of this structure to that of perovskite, which was missed in the previous work, is sufficiently important to be

[a] School of Chemistry and EaStChem, University of St Andrews, St Andrews, Fife, KY16 9ST, U.K. E-mail: pl@st-and.ac.uk

‡Electronic Supplementary Information (ESI) available: Experimental details, PXRD, TGA, FTIR data, distortion mode analysis, crystallographic data (CIF). CIF data have been deposited with CSD: deposition number CSD 1503284.
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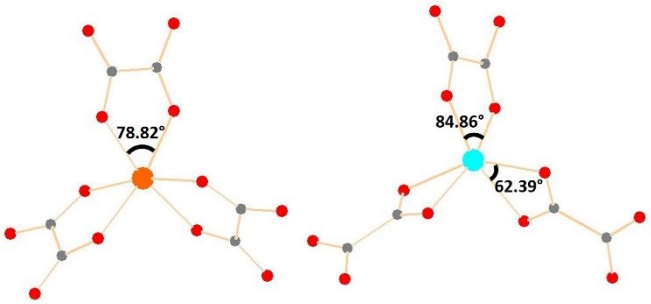

Figure 2. Coordination modes of the Fe^{2+} (left) and Li^{+} (right) sites. Fe-O bond lengths 2.1229(17) Å; Li-O bond lengths 2.021(5)-2.178(4)Å, O-B-O bite angles are displayed in the figure.

described in detail in the present work. This new insight may lead on to the targeted design of related compositions and structural variants with potential for novel functionalities.

The first essential feature of the crystal structure is an extended 3-D network of corner-linked LiO_6 and FeO_6 octahedra (Fig. 1). Each of the oxygen atoms of the oxalate group acts as a single-atom bridge between adjacent Li and Fe centres, such that if the carbon atoms are removed from the representation, the perovskite-like framework can be clearly seen. The behaviour of the oxalate group therefore contrasts with that of the formate group in the well-established hybrid perovskite family, which form a perovskite-like framework *via* extended M-O-C-O-M links. In the present case, the carbon atoms are not a necessary component of the 3-D framework, but play a secondary role in bridging near-neighbour and next-near-neighbour octahedra. Structurally, the framework may therefore be viewed as a mixed metal oxide, 'decorated' by the additional C-C connections. In more detail, it can be seen that the LiO_6 and FeO_6 octahedra form a long-range ordered array in a 3:1 ratio such there are Li-O-Li and Li-O-Fe but no direct Fe-O-Fe links. Such an ordering pattern of the B-site species in a conventional perovskite has been seen, for example, in $Ba(M_{0.25}Sb_{0.75})O_3$ (M = Li, Na)[2,12]. The second feature of the cation ordering is that the K^{+} cations occupy only ¼ of the available perovskite-like A-sites; again this occurs in a fully-ordered array, and has a parallel in conventional perovskite chemistry in compounds such as $CaCu_3Ti_4O_{12}$[13]. However, the combination of 1:3 ordering patterns at the A and B sites *simultaneously* has not been seen previously. The $CaCu_3Ti_4O_{12}$ family has examples of 1:3 A-site order with 1:1 B-site order, for example in $CaCu_3Fe_2Sb_2O_{12}$[13].

Locally, the coordination around each of the octahedral B sites consists of three μ_2 oxalate groups, though the coordination mode differs between the two. The iron is coordinated to six symmetry-related O1 atoms from different carboxylate groups of each oxalate, forming three identical five-membered chelate rings, while Li is surrounded by four O1 and two O2 atoms from three symmetry-related oxalate ligands, constructing one five-membered ring, as in the case of Fe, and two four-membered rings by connecting to both O atoms of carboxylate group of each oxalate (Fig. 2). This consequently leads to severe distortions to the Li environment in the LiO_6 octahedral units. A quantitative measure of octahedral distortion is given by the distortion parameter Δ and bond angle variance δ^2, defined as

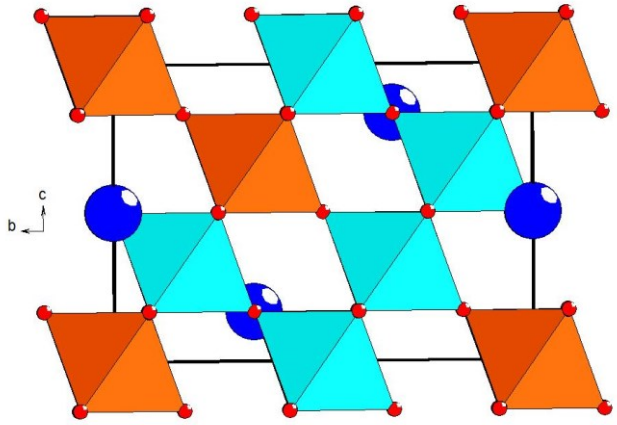

Figure 3. Hypothetical perovskite with simultaneous 1:3 cation order at the A and B sites (compare to Fig. 1). This model is derived by symmetry mode analysis, as described in the text.

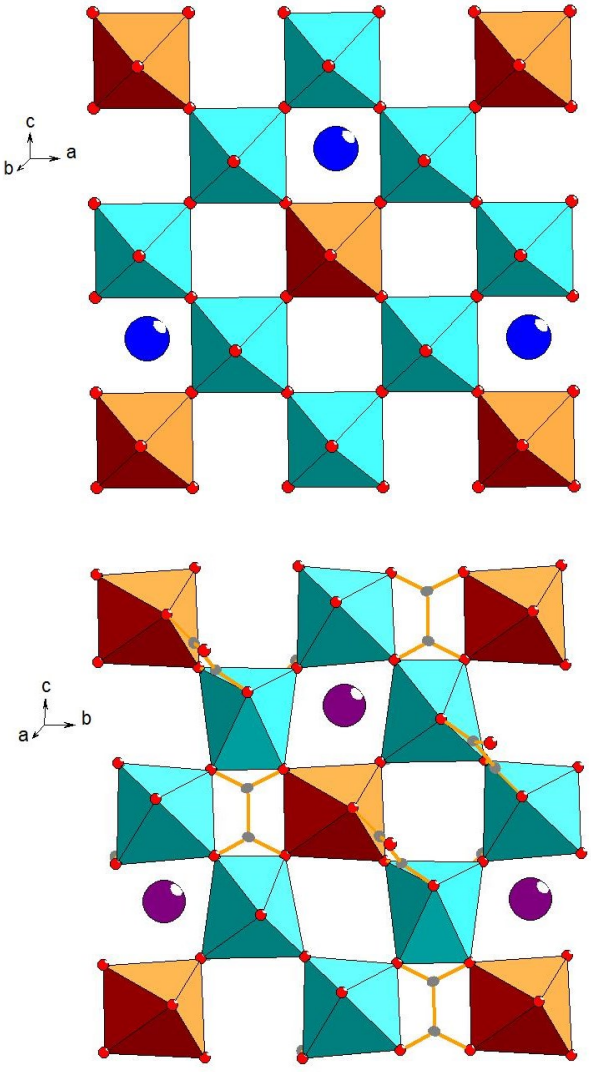

Figure 4. View along a direction equivalent to the [100] of the parent cubic perovskite: (above) hypothetical 1:3 ordered perovskite (as in Fig. 3), and (below) $KLi_3Fe(C_2O_4)_3$. In each case, only K atoms above the plane of the BO_6 octahedra are shown.

$\Delta = 1/6 \sum_{n=1-6}[(d_n - d)/d]^2$ and $\delta^2 = 1/11 \sum_{i=1-12}(\theta_i - 90)^2$ where d_n stands for nth bond length, d for average bond length and θ for bond angle.[14-15] In title compound, Δ and δ^2 correspond to zero and 43.93 for FeO_6, and 4.16×10^{-3} and 197.66 for LiO_6, respectively. The K^+ cation at the A-sites has a relatively regular 12-coordinate geometry with K-O bond lengths of 6 × 3.0097(19) and 6 × 3.1830(18) Å. Bond valence sum (BVS)[16] calculations reveal values of +2.08, +1.08, +1.09, for Fe, Li, K atoms, respectively.

Using the on-line crystallographic tool ISODISTORT[17], idealised models for different combinations of A-site and B-site ordered perovskites can easily be derived. ISODISTORT uses symmetry-adapted normal modes to represent particular types of structural distortion from a high symmetry parent phase; in this case the aristotype cubic perovskite with B at (0,0,0). Here, the relevant modes are described by irreducible representations M_1^+ for the B-site ordering and M_4^+ for the A-site ordering.

Simultaneous activation of both these modes leads to several superstructures displaying simultaneous A-site and B-site cation ordering. The simplest model that allows 1:3 ordering at both the A and B sites is found to have a unit cell of dimensions $a \sim 2\sqrt{2}\ a_p$, $c \sim \sqrt{3}\ a_p$ and $V = 12\ V_p$, relative to the aristotype cubic perovskite ($a_p \sim 4$ Å); and space group $R\bar{3}m$, hexagonal setting (see ESI for further details). This idealised cation-ordered perovskite structure, which has not been seen in practice, is shown in Fig. 3. The title compound has an additional superlattice relative to this ideal, cation-ordered perovskite such that $c' \sim 2c$, and the space group changes from $R\bar{3}m$ to $R\bar{3}c$. This additional superlattice arises from the accommodation of the oxalate groups in 'alternating' fashion, relative to the octahedral edges, along the c-axis. A comparison of the structure of the title compound, alongside that of the hypothetical cation-ordered structure of Fig. 3, is shown in Fig. 4. In this case the structures are viewed down the pseudo-cubic [100] direction so that the relationship to the conventional perovskite and the nature of the unique 1:3 / 1:3 cation-ordering, can be more clearly seen.

The stoichiometry and composition of the title compound, when regarded as a 'perovskite' are clearly highly unusual. For an oxide perovskite, ABO_3, the cationic charges must sum to 6+, and for a halide ABX_3, to 3+. In this oxalate derivative, reduced to an empirical formula "$K_{0.25}(Li_{0.75}Fe_{0.25})(C_{1.5}O_3)$", the charges sum to only 1.5+; i.e. the oxalate, with all O atoms acting as bridging ligands, effectively reduces the charge at the X site to 0.5-. From this, there appears to be little direct scope for tuning the composition of this structure type beyond varying the cation size of the monovalent and divalent cations at the A and B sites. However, an A-site vacant derivative, "$B^I_2B^{II}_2(C_2O_4)_3$", could incorporate up to 50% divalent cations at the B-site, which may allow for increased functionality in terms of magnetic or electronic properties. Moreover, other possibilities for extending this structure type into a wider family of 'oxalate-perovskites' certainly exist. For example, reducing the oxalate content such that only two of the six X ligands in each BX_6 octahedron are contributed by oxalate, leaving the other positions available as oxide, halide etc. (e.g. keeping the 'in-plane' ligands only, shown in Fig. 4b) may lead to an extended family of 3-D perovskites. Other options may include layered perovskite analogues (e.g. "ABX_4" or "A_2BX_4" types) designed by suitable combinations of oxalate and other anionic moieties. Variants such as this may lead to enhanced prospects for functionality such as ferroelectricity, magnetic ordering or ionic conductivity within a wider family of oxalate perovskites.

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